Opponent's opinion

Disertation thesis:
Kinetics of processes in the volume and at the surface of amorphous materials
Author: **Ing. Diego Alejandro Valdés Mitchell**

In the presented dissertation, in a form of annotated publications, the author deals with the preparation and characterization of bulk chalcogenide glasses and their thin films such as a-Se, Se-Te system and binary system $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ (from $x = 0.4$ to 0.9). In this thesis, an exhaustive study of the crystallization behavior in these chalcogenide glass-forming materials is presented. Crystallization process was analyzed combining several methods such as microscopy techniques (infrared, optical, AFM, scanning electron microscopy-SEM), methods of thermal analysis (DSC, TMA, PAMFT) and methods of structural analysis (XRD).

Part I (Chapters 1 to 4) are designed to bring necessary theoretical background and understanding and meaning to further text and work.

Part II (Chapter 5. Experimental part, Chapter 6. Paper synopsis.)
The main focus of this dissertation were divided into two parts. The first part is focused on the extensive study on crystal growth in different samples of amorphous Se and $Se_{95}Te_5$, which is supported with viscosity measurements in $Se_{95}Te_5$ melts. Together these works bring a new insight into the competing volume and surface crystal growth with respect to the viscosity and surface diffusion in Se and $Se_{95}Te_5$ glass formers.
For selenium samples it was possible to state conclusion that the crystal growth kinetics in thin films and at the surface of bulk samples of a-Se is controlled by the surface diffusion rather than by the viscous flow.
The crystal growth mechanism in $Se_{95}Te_5$ thin films is comparable to the crystal growth mechanism at the surface of Se bulk samples.
The second part is dedicated to the crystal growth in $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ glass formers. In this part, a direct study of the crystal growth kinetics in the $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ system and its relation to the viscous flow and diffusion was presented. Two types of crystal growth mechanisms were observed. The surface crystal growth kinetics of both Sb_2Se_3 and $GeSe_2$ phases in all the compositions, presented a strong decoupling from the Stokes-Einstein relation.

The work is very well and carefully written, both factually and formally, with a traditional division into a form of text such as annotated publications.

One can perhaps only complain about omitted information about the condition of some experiments related to conditions of crystal growth in thin films and bulks. I was not able to find in the text information about the preparation of samples for monitoring the growth of crystals in their volume and on the surface of bulk samples.

On the contrary, it can be stated with respect that the author mastered a number of experimental techniques, both theoretically and practically, which he used appropriately to characterize thermal and structural properties.

Questions:

Q1: For in-situ experiments, the studied samples were deposited on glass substrate? Have you tested any other substrates to avoid any contamination from the substrate?

Q2: For in-situ experiments, the studied samples were placed into the heating stage and during the sample's annealing the crystal growth was recorded. Has been done annealing of samples in inert atmosphere and under illumination by light from microscope?

Q3: Has been done there any XPS studies to exclude any influence of surface oxidation which could lead to SeO_2 growth on the Se surface?

Q4: Please, explain process of transition from diffusion-controlled to diffusionless crystal growth.

From the submitted thesis and from the overview of publishing activities (5 articles in foreign peer-reviewed journals) with a number of valuable citation responses, active participation in foreign and domestic conferences and participation in grant projects, it follows that ing. Valdéz fully meets all prescribed framework criteria for successful defense of the dissertation.

Disertation thesis of ing. Ing. Diego Alejandro Valdés Mitchell is excelently processed, it meets all professional criteria, and therefore I recommend accepting it for the defence and award of the PhD degree.

[redacted]

V Pardubicích, 14. 1. 2022

prof. ing. Tomáš Wágner, DrSc.